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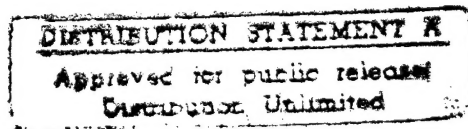
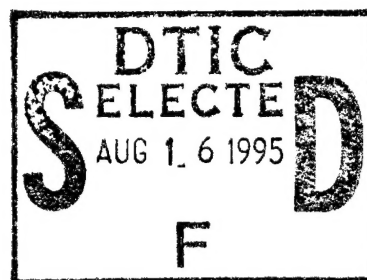
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CHEMICAL PROCESS TO RECOVER URANIUM  
FROM PHOSPHATE ROCK

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January 15, 1948

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Topical Report

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TOPICAL REPORT

on

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FROM PHOSPHATE ROCK

Prepared by

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SUMMARY

This topical report describes progress made in chemical dissolution and recovery of uranium from phosphate rock. It covers approximately the period from November 15, 1947, to January 15, 1948, but the figures and other data are in part based on investigations since the start of this project.

Two outstanding developments are: (1) an increase in the dissolution of uranium from the rock with sulphuric acid from about 55 per cent to about 85 per cent and (2) an increase in recovery of uranium from solution from about 50 per cent to 90 to 95 per cent. The increase in dissolution was obtained by calcining the rock prior to leaching. The better recovery resulted from use of larger amounts of amine in the precipitation. The indicated over-all recovery, not yet fully worked out on solutions from calcined rock, is about 80 per cent.

The use of increased amine raises the problem of recovery and re-use of this reagent. This is being studied.

Tentative beaker-stage schematic flow sheets for the most promising of the other leaching and precipitation processes are given in the text.

### RAW MATERIALS

No additional phosphate rock or superphosphate samples were received since the topical report of November 15, 1947, was written. Additional chemical analyses of some of the materials listed in Tables 1 and 2 of that report have been made and are given in Table 1 of the present report.

### SULPHURIC ACID LEACHING OF CALCINED ROCK

In Table 5 of the topical report for November 15, 1947, extractions of 83 and 84 per cent of the contained uranium are reported when the rock was calcined prior to leaching with sulphuric acid. These experiments were repeated on Idaho Rock No. 1090-8 and extended to Florida Rock No. 1090-18. The results are given in Table 2.

In the earlier experiments, the rock was roasted at 1290°F. (700°C.) for 24 hours and in the present ones at 1560°F. (850°C.) for 2 hours.

The uranium extraction from the Idaho rock ranged from 77 to 84 per cent. This is an increase of about 20 per cent over the extraction obtained from the raw rock. The variation in time and temperature of roasting did not seem to change the extraction. Acid concentrations from 24 to 72 per cent, likewise, effected about the same extraction.

The uranium extraction from the Florida rock was 87 per cent with diluted acid and 50 per cent with 72 per cent acid used in superphosphate

TABLE 1. COMPOSITION OF SOME PHOSPHATE ROCKS AND SUPER-PHOSPHATES ON HAND JANUARY, 1948

(Supplementary to Tables 1 and 2 in the Topical Report for November 15, 1947).

Number	Received	U	Composition, %		Nature	Source(1)
			Total	P2O5		
				Available		
<u>Phosphate Rocks</u>						
1090-50	Oct., 1947	0.014	-	-	Washed pebble	Virginia-Carolina, Nichols, Florida
-51	Ditto	0.011	-	-	Flot. conc.	Ditto
-54	"	0.013	-	-	Ground rock	"
<u>Superphosphates</u>						
1090-28	July, 1947	0.008	20.8	-	Run of pile	Davison, Curtis Bay Plant, supposedly de- rived from Rock No. 1090-30
-29	Ditto	0.009	21.5	-	Granulated	Ditto
-55	Oct., 1947	0.008	20.5	19.8	-	Virginia-Carolina, Nichols, Florida
-56	Ditto	0.008	20.5	19.5	-	Ditto

(1) Virginia-Carolina is Virginia-Carolina Chemical Corporation.  
Davison is Davison Chemical Corporation.

TABLE 2. THE EFFECT OF CALCINING OF THE PHOSPHATE ROCK ON SUBSEQUENT URANIUM DISSOLUTION

Basis: 100 g. of original phosphate rock

1090-18 - International Minerals and Chemical Corporation. Uranium content - 10 mg.

1090-8 - Geological Survey sample from Idaho. Uranium content - 13 mg.

1090-18 after roast weighed 97.7 g.

1090-8 after roast weighed 93.7 g.

Test No.	Phosphate Rock No.	H <sub>2</sub> SO <sub>4</sub> Conc., %	Per Cent of Theoretical (1)	Uranium Extracted	
				mg.	%
<u>Roasted at 1560°F. (850°C.) for 2 Hours</u>					
2940-61-5	1090-8	72	100	12.2	94
-6	-8	24	100	10.2	77
-7	-18	72	100	5.0	50
-8	-18	24	100	8.7	87
<u>Roasted at 1300°F. (700°C.) for 24 Hours</u>					
2758-72-1	1090-8	24	94	10.7	83
-73-1	-8	(2)	94	10.9	84

(1) Based on that required to make superphosphate.

(2) Dorr acid: 22% H<sub>2</sub>SO<sub>4</sub>  
16% H<sub>3</sub>PO<sub>4</sub>



manufacture. The extraction with diluted acid was two to three times as great as was obtained by water leaching superphosphate made from the raw rock.

Data are now being obtained on uranium recovery from these leach solutions. In general, the solutions were much more acid than those obtained by water leaching superphosphate. Barring unforeseen factors, however, the recovery of uranium by amine precipitation, after possible adjustment of acid in the leaching or of pH after leaching, should be possible, as shown by the results on superphosphate solutions.

#### AMINE PRECIPITATION OF URANIUM FROM SUPERPHOSPHATE LEACH SOLUTIONS

The amount of AM Coca B (Armeen CD) used in the precipitation of uranium from superphosphate leach solutions until recently had been restricted to small amounts, i.e., less than one gram of amine per 400 cc. of leach solution. The maximum precipitation of uranium obtained with this amount of amine was about 50 per cent of that in the solution. Further tests were made in a leach solution from Superphosphate No. 1090-20 with up to 10 grams of amine per 400 cc. of leach solution, or a ratio of 2175 parts of amine to 1 part uranium. This amount swept over 90 per cent of the uranium from the solution. The results of the tests are presented in Figure 1. Corresponding tests have been made on leach solutions from the other superphosphates, but analytical results have not been received.

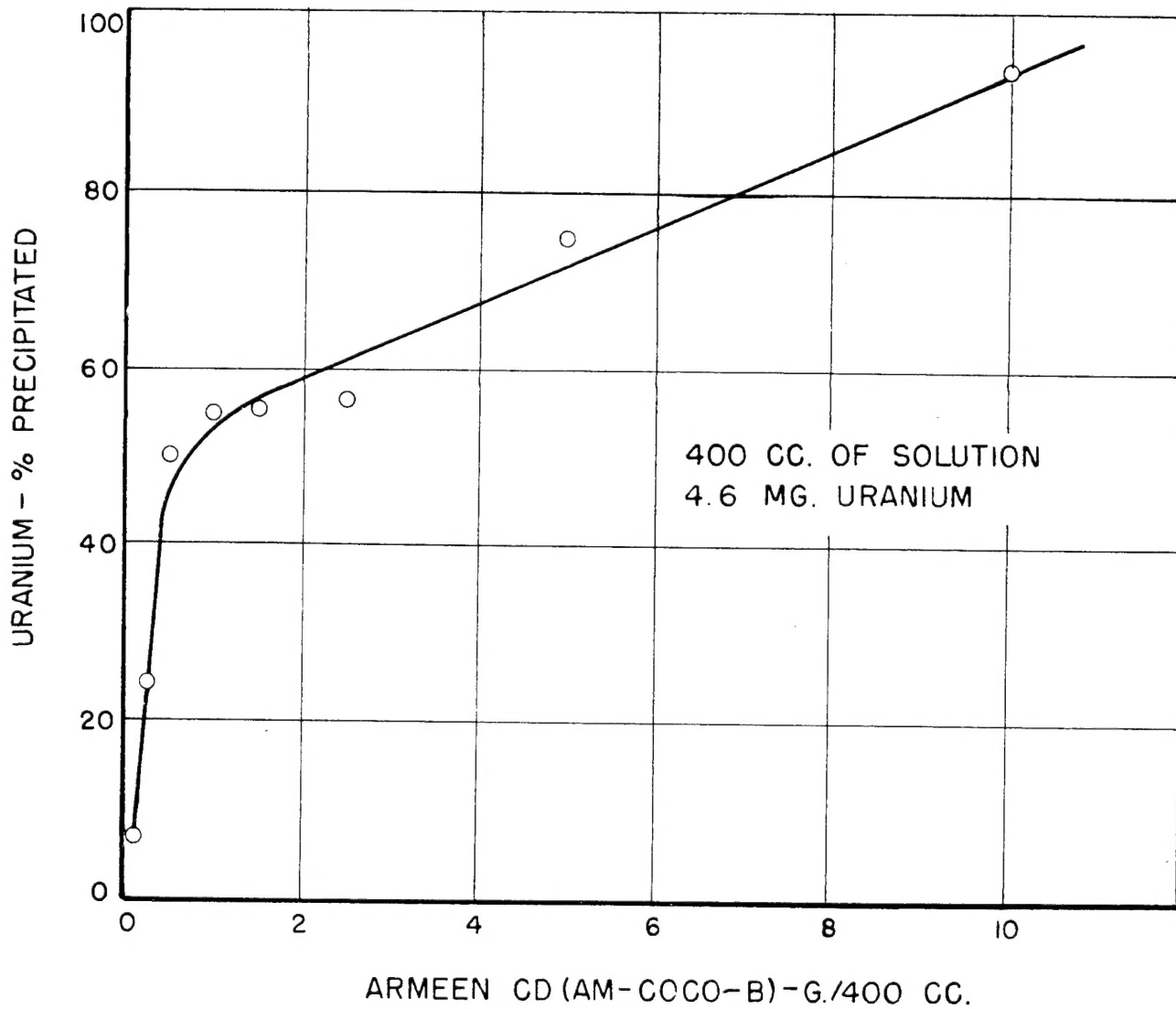


FIGURE I. PRECIPITATION OF URANIUM FROM WATER LEACH SOLUTION FROM SUPERPHOSPHATE NO. 1090-20.

The precipitation curve is almost linear up to a ratio of 0.5 gram of amine per 4.6 mg. of uranium. At this point, about 50 per cent of the uranium was precipitated. Beyond this point the slope changed so abruptly that it took 9.5 grams of amine to precipitate most of the remainder. Nevertheless, the series demonstrates that it is possible to remove practically all of the uranium from solution by this means.

The use of a large ratio of amine to uranium presupposes some means for recovering the amine and using it over again. Such methods are being sought.

#### POSSIBLE PROCESS FOR URANIUM AND $P_2O_5$ RECOVERY

In Figures 2 and 3 are sketched possible flow sheets for uranium and  $P_2O_5$  recovery in a process for leaching calcined phosphate rock with sulphuric acid. In evaluating these data, it should be borne in mind that they are based on beaker-scale work and, therefore, do not represent an actual process. They serve merely for discussion to show typical flow sheets that should be investigated on a test-plant scale.

The scheme in Figure 2 envisages calcining phosphate rock in order to make it more amenable to leaching. The calcined rock is then leached with dilute sulphuric acid to dissolve the uranium and  $P_2O_5$ . A dissolution of over 80 per cent of the uranium and over 90 per cent of the  $P_2O_5$  has been obtained. The residue, after washing, is retained and the solution treated for the recovery of the uranium and  $P_2O_5$ . The uranium is

FIGURE 2. SULPHURIC ACID TREATMENT OF CALCINED ROCK

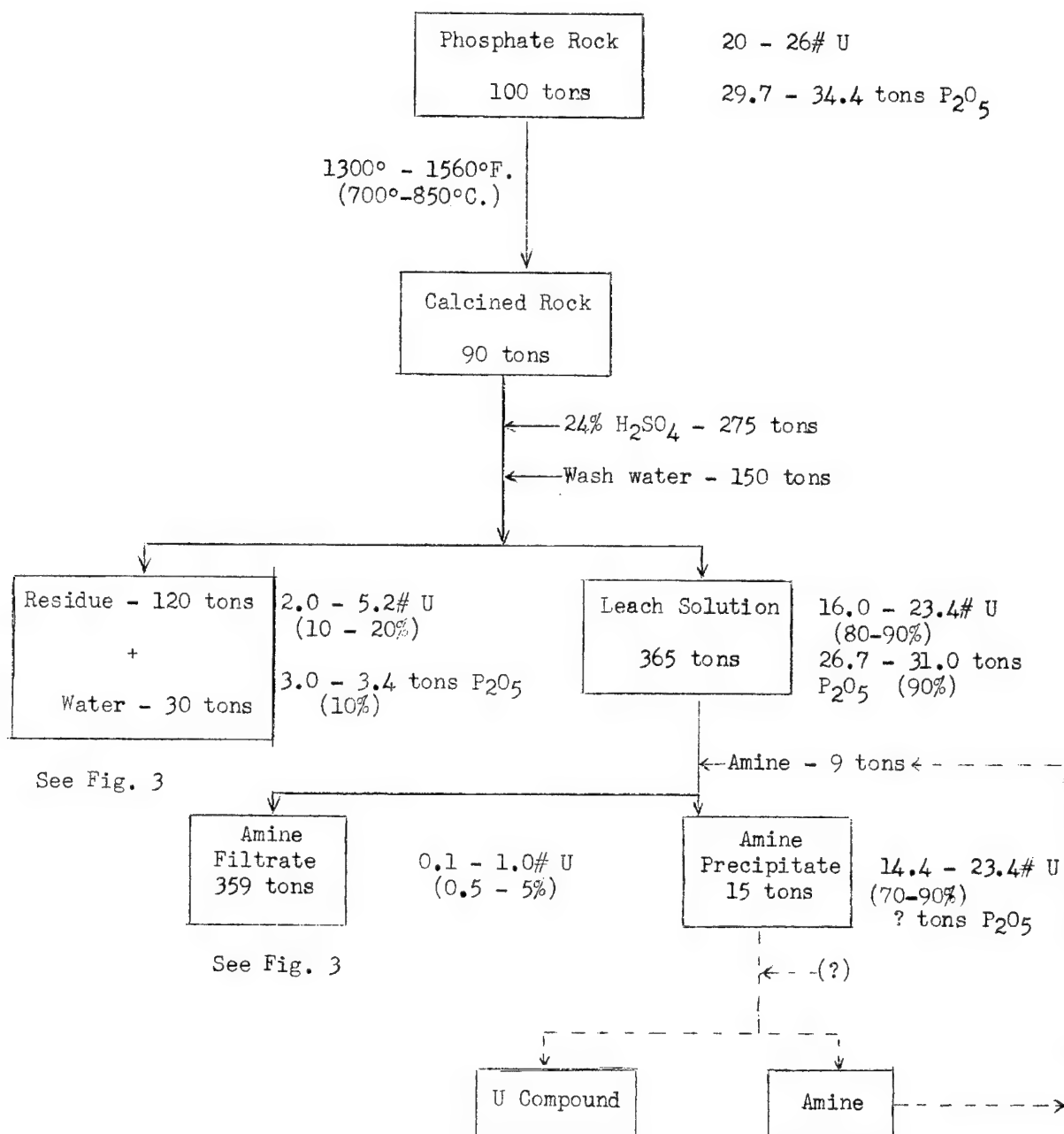
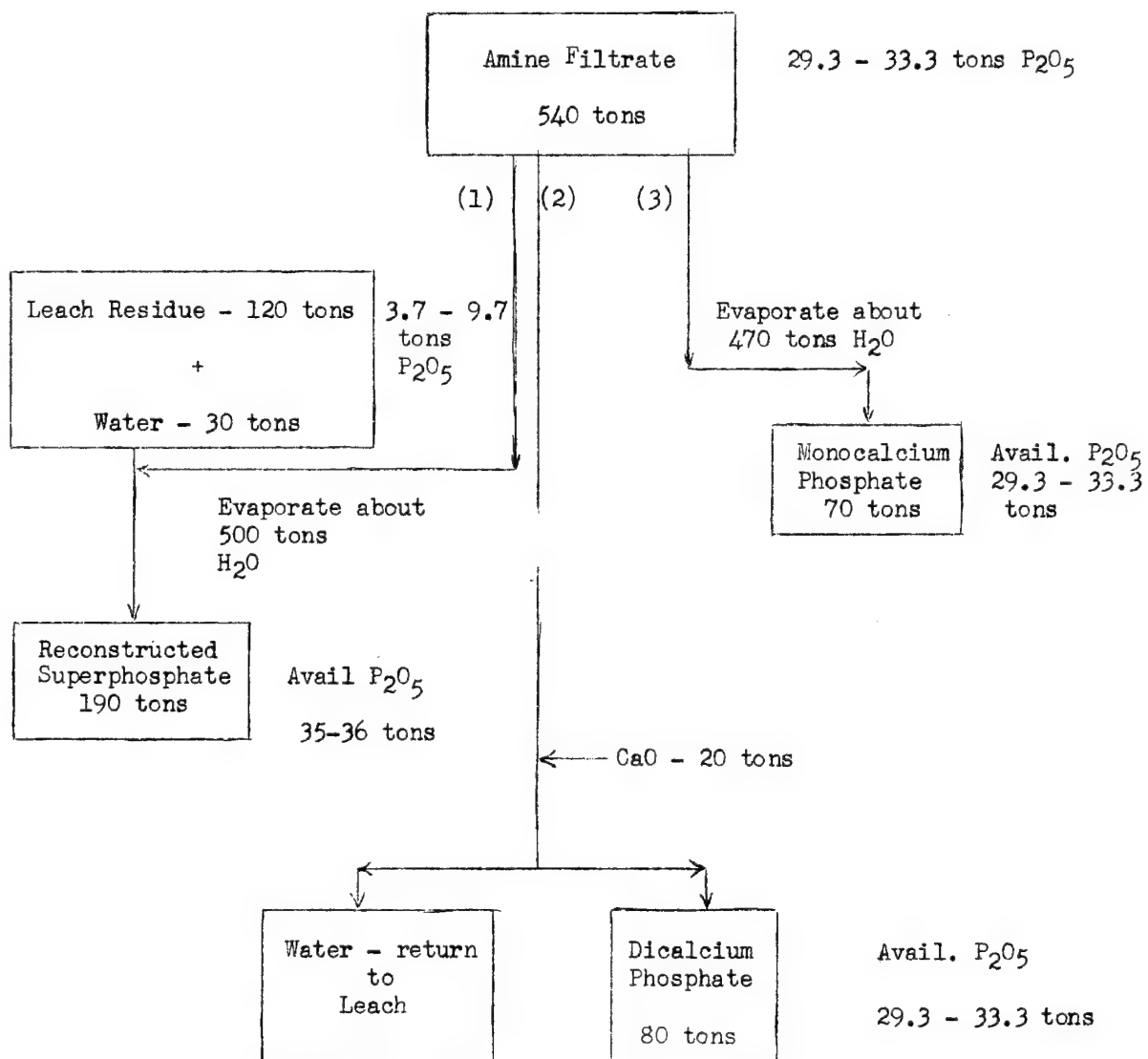


FIGURE 3. RECOVERY OF  $P_2O_5$



precipitated with a coconut oil amine. In the laboratory, up to about 95 per cent of the uranium has been recovered from superphosphate leach solutions by this method.

Figure 3 indicates three possible ways of recovering the  $P_2O_5$ . They are, briefly: (1) evaporation of the amine filtrate in contact with the leached residue to reconstruct superphosphate, (2) precipitation of the  $P_2O_5$  from the amine filtrate with  $CaO$  to make dicalcium phosphate, and (3) evaporation of the amine filtrate to make monocalcium phosphate. By all three methods, high-grade products were obtained in the laboratory.

#### OTHER PROCESSES

Other possible processes include (1) leaching superphosphate either with or without a preliminary acid treatment, (2) acid leaching of the rock with sulphuric acid or some other acid, and (3) treatment of the leached residue from superphosphate or from phosphate rock for uranium. All of these have been studied on a beaker scale in the laboratory. They are included for discussion purposes.

#### Uranium Recovery From Commercial Superphosphate by Water Leaching and Amine Precipitation

Six commercial superphosphates from various sources(1) were leached with water. Two of these were also leached after pretreatment with

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(1) Compositions, sources, and other data are given in Tables 1 and 2 of the Topical Report for November 15, 1947, and in Table 1 of the present report.

sulphuric acid. The general features and results of such extraction of uranium and  $P_2O_5$ , and recovery of the uranium by amine precipitation, are shown in the flow sheets in Figures 4 and 5. As can be seen, the over-all recovery of uranium under optimum conditions was a little over half of that which was obtained when the rock was calcined before leaching.

Included in the six superphosphates was a granulated product. Water extraction of uranium from this was only about one-third to one-fifth as great as from the other materials.

Uranium Recovery From Raw Phosphate Rock by  
Sulphuric Acid Leaching and Amine Precipitation

In Figure 6 are summarized beaker data on recovery of uranium from raw phosphate rock with sulphuric acid and amine precipitation. Leaching with dilute acid and laboratory preparation and leaching of superphosphate are both shown.

In general, the uranium dissolution with dilute acid was a little higher than was obtained by making and leaching superphosphate or by leaching commercial superphosphate. The over-all recovery was, however, considerably lower than in the calcined-rock process.

Uranium Dissolution From Raw Phosphate  
Rock With Phosphoric Acid

Figure 7 shows data obtained by making triple superphosphate from one Idaho rock and three Florida rocks and leaching with water. The uranium extraction ranged from 35 to 85 per cent. It was not uniform even

FIGURE 4. LEACHING COMMERCIAL SUPERPHOSPHATE (WATER)

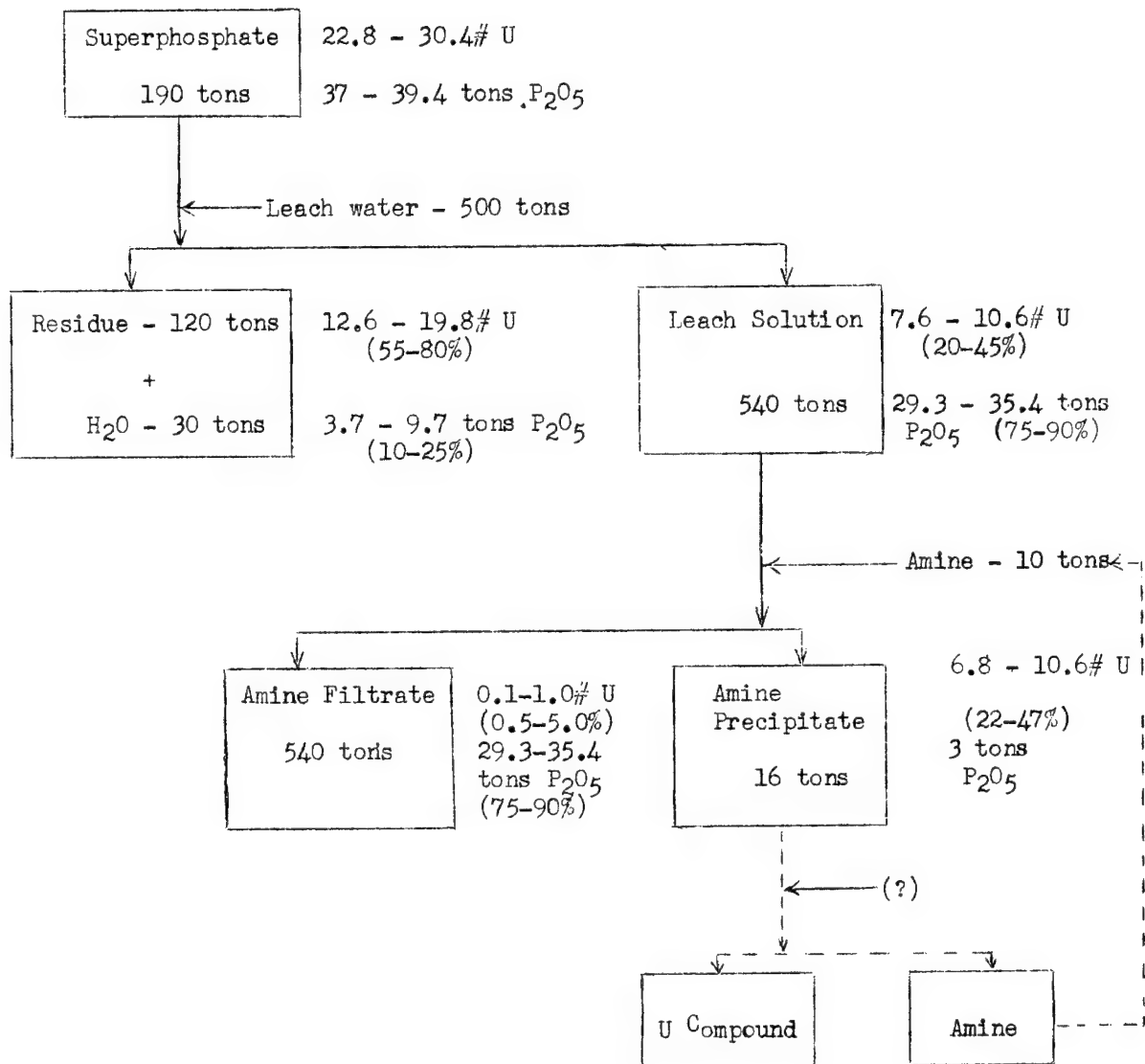




FIGURE 5. LEACHING COMMERCIAL SUPERPHOSPHATE (ACID PRETREATMENT)

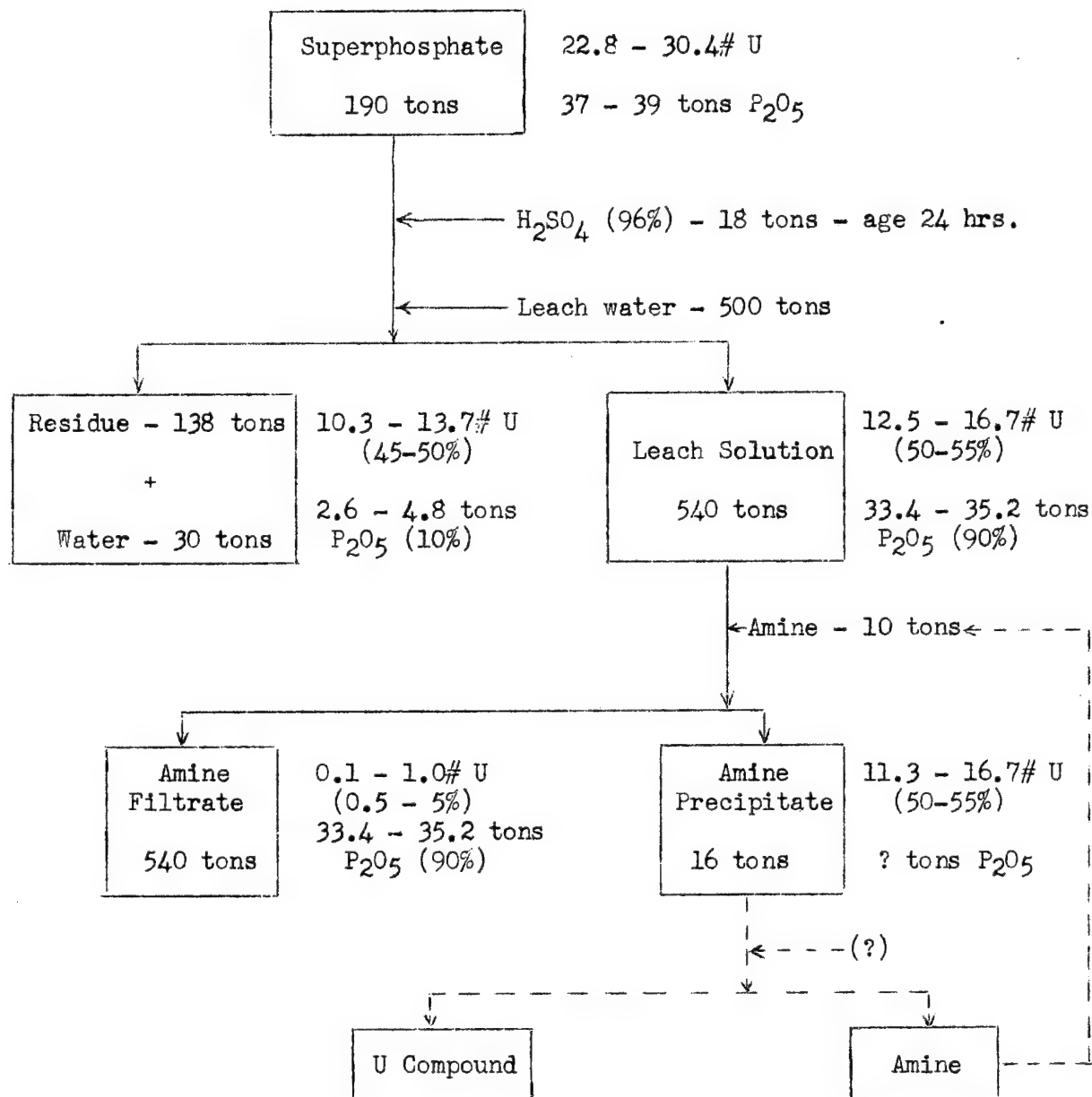


FIGURE 6. SULPHURIC ACID TREATMENT OF RAW PHOSPHATE ROCK

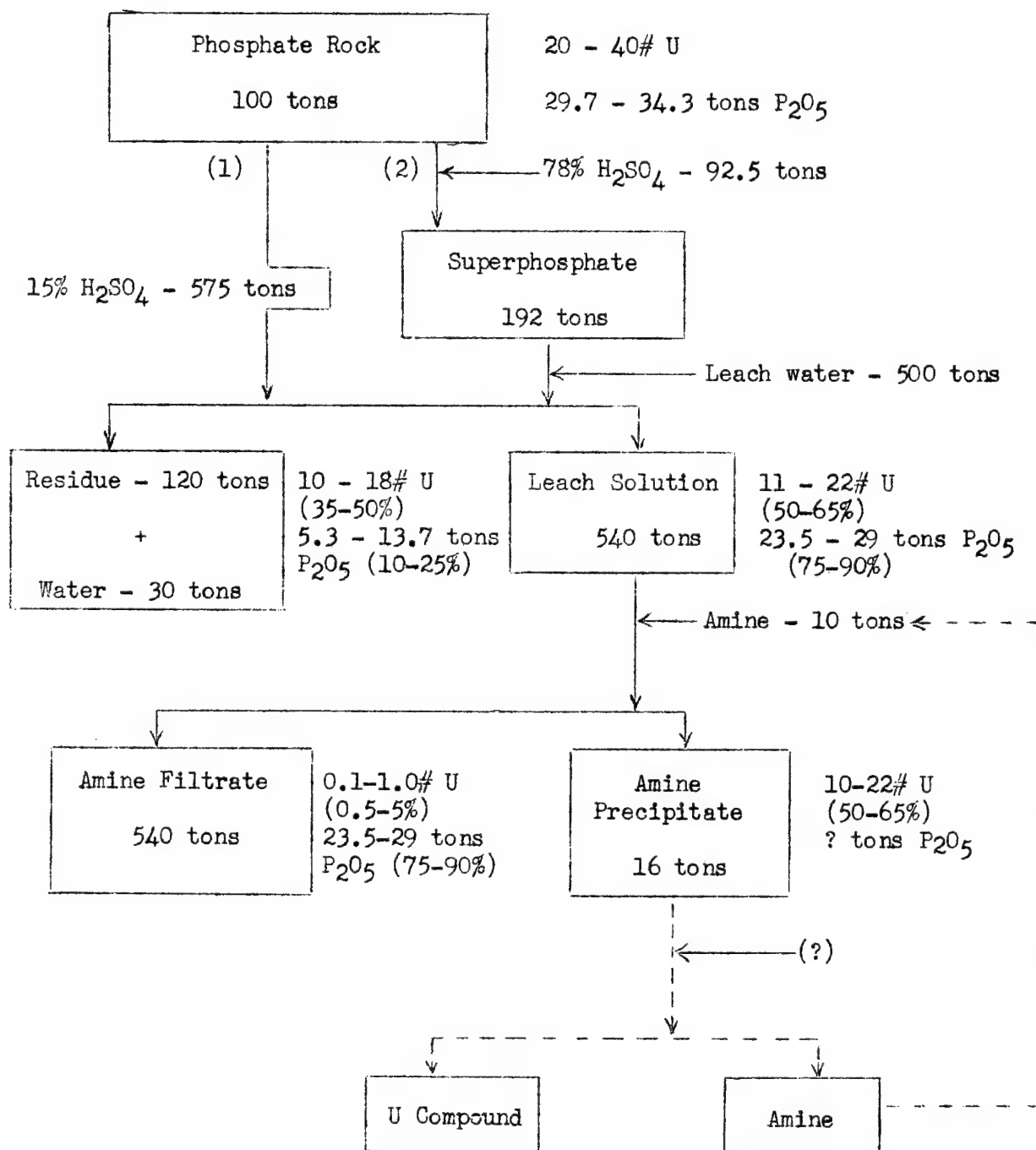
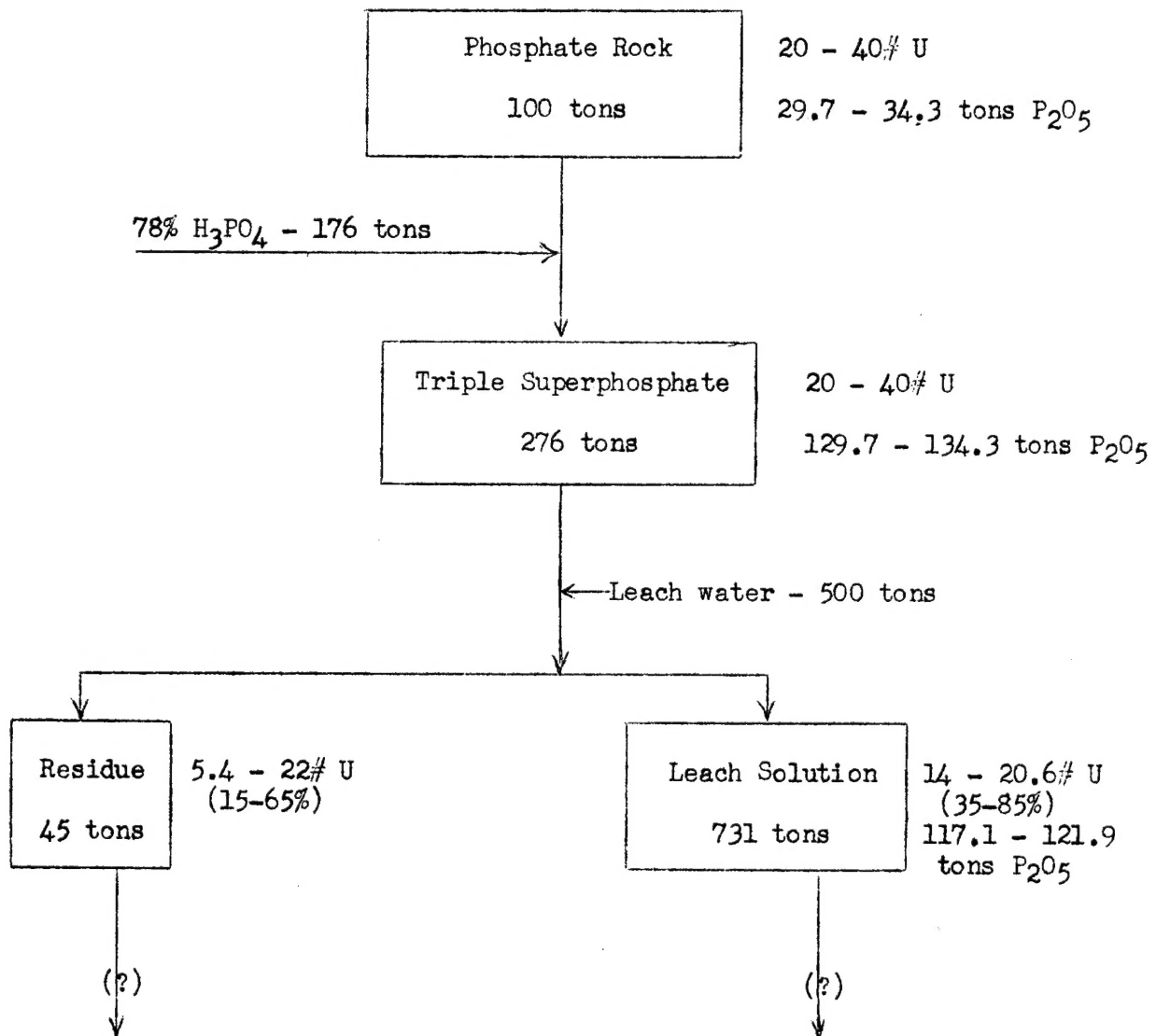


FIGURE 7. PHOSPHORIC ACID TREATMENT OF PHOSPHATE ROCK



on rocks from the same region, so that there is still considerable uncertainty about how much can be extracted. The data indicate inferior results to the calcined rock process.

#### Uranium Recovery From Leached Superphosphate Residues

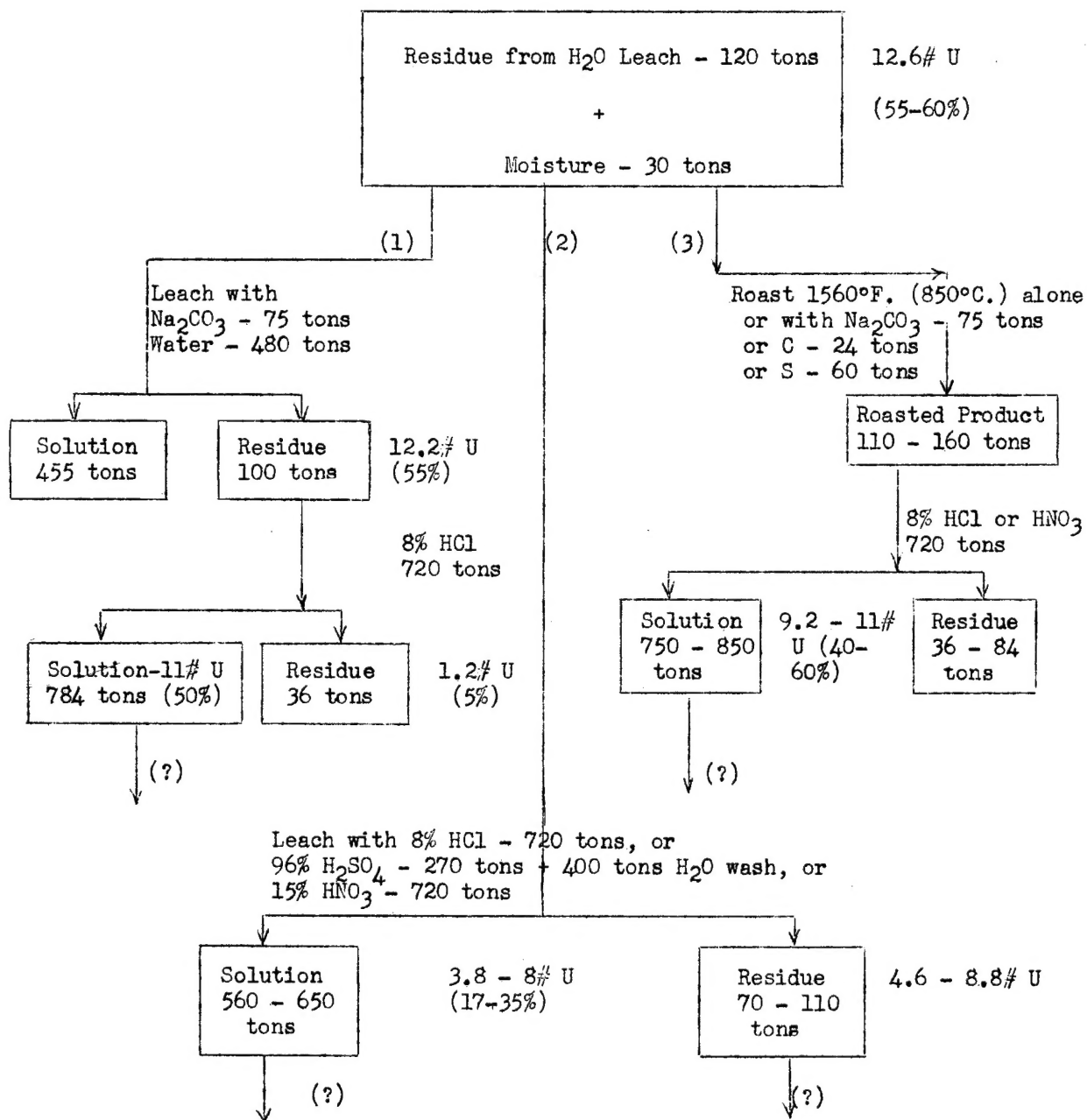
Water-leached superphosphate residues generally retained more than half of the uranium. Figure 8 shows schematically various beaker-stage processes for removing uranium from such residues. The best process at the moment appears to be one in which the residue is roasted at 1560°F. (850°C.) and leached with dilute hydrochloric or nitric acid. By this means, 93 per cent of the uranium in the residue (57 per cent of that in the original superphosphate) was dissolved. Details of the other processes may be seen in Figure 8.

Recovery of uranium from the solutions has not yet been attempted.

#### FUTURE WORK

Immediate effort will be placed on the calcined-rock process. The process will be carried through all the steps from calcination of the rock to recovery of amine, uranium, and  $P_2O_5$ . Of particular importance are (1) determination of optimum calcination times and temperatures, (2) amounts of acid and concentration, (3) amount of wash water, (4) amount of amine, and (5) methods of recovery of amine and uranium.

FIGURE 8. RECOVERY OF URANIUM FROM LEACH RESIDUE



Recovery and re-use of amine are highly important to the economic success of the process because of the large amounts of amine required. Methods for recovery and re-use will receive major attention.

The process will be studied on a larger scale almost immediately. The larger scale work contemplated at the moment will consist of tests on 50-pound samples of rock. The process will be carried through batchwise on all of the various steps.